



Overcharge Protection in Ambient Temperature Lithium and Lithium-Ion Cells:

A Literature Survey

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Overcharge Protection in Ambient Temperature Lithium and Lithium-Ion Cells: A Literature Survey

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Abstract

This report summarizes a survey of the literature on in situ electrochemical methods to provide overcharge protection in ambient temperature lithium and lithium-ion cells. Among the various rechargeable lithium battery systems, only the lithium cells using solutions of inorganic salts such as LiAlCl_4 or LiGaCl_4 in sulfur dioxide as electrolytes were found to have inherent overcharge protection. For low-voltage lithium cells such as lithium/titanium disulfide, the survey identified a number of electrolyte additives that undergo oxidation above the charging potentials but below the solvent oxidation potential and can provide overcharge protection in these cells. The oxidized form of the additive then reacts with lithium to regenerate the original electrolyte additive. However, no suitable electrochemical method was identified for providing overcharge protection in lithium or lithium-ion cells that require charging to potentials above ~ 4 V.

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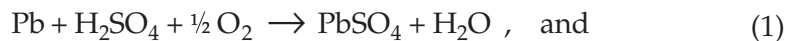
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1. Introduction

Overcharge protection in rechargeable batteries is essential for safe battery operation in various military and commercial applications. Overcharge protection can be accomplished electronically. This involves monitoring the voltage of individual cells in a battery with feedback to the charger. This approach, now the only one available for lithium and lithium-ion batteries, has two main drawbacks. First, it involves increased expense and complexity. Second, such monitoring of individual cells is limited in its ability to discern the state of charge (SOC) from cell voltage. Cell voltage, an indirect measure of cell SOC, can be inaccurate and (in the event of imperfections) sometimes grossly misleading. Reliance on cell voltage, therefore, requires significant derating of cell capacity.

A far superior approach to overcharge protection is the use of a chemical mechanism in the cell that can absorb the excess charge during charging operations without irreversibly altering or degrading any cell component. This is the area reviewed in this report. Two of the most widely used battery systems—lead-acid and nickel-cadmium—inherently possess an overcharge protection mechanism and can accept large amounts of overcharge during charging operations. Over the years, attempts have been made to devise such a mechanism for the newer lithium and lithium-ion batteries.

In lead-acid batteries [1,2], overcharge results in the production of hydrogen and oxygen gases and the subsequent loss of water. Oxygen reacts with lead at the negative electrode, and hydrogen is oxidized at the lead dioxide positive electrode in the presence of sulfuric acid, according to the following recombination reactions, respectively:



The lead-acid batteries are designed to promote the recombination reaction so that the excess charge during charging operations is absorbed by the cell without causing any undesirable changes in the battery.

Nickel-cadmium batteries [3] are designed so that the negative cadmium electrode has a higher capacity than the positive nickel oxyhydroxide electrode. During charge, the positive electrode reaches full charge and begins to evolve oxygen that migrates to the negative electrode and reacts with cadmium to form cadmium hydroxide, according to the reaction



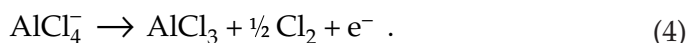
The transfer of oxygen to the negative electrode is promoted by the use of a separator that is permeable to oxygen and by the use of a limited amount of electrolyte. Thus, like lead-acid batteries, any overcharge is absorbed by the cell without deleterious effects.

Unlike lead-acid and nickel-cadmium batteries, lithium and lithium-ion batteries (except for a lithium/SO₂ rechargeable battery system) have no inherent overcharge protection. The excess charge leads to the deposition of lithium at the negative electrode and the oxidation of the solvent at the positive electrode. The solvent oxidation results in the degradation of the electrolyte and causes premature failure of lithium and lithium-ion cells. The deposition of dendritic lithium at the negative electrode contributes to the safety hazards of these cells. Therefore, a number of attempts have been made to find electrolyte additives for lithium cells that would be oxidized at potentials higher than the potentials used to charge the positive electrode but lower than the solvent oxidation potential. Further, the oxidized form of the additive would then react with excess lithium to regenerate the original additive. The electrolyte additive would thus provide an electrochemical shuttle mechanism in lithium and lithium-ion cells during overcharge operations that would absorb the excess charge and provide overcharge protection.

The purpose of this report is to survey the literature and summarize all the attempts that have been made to provide overcharge protection in lithium and lithium-ion cells.

2. Lithium Cells With Inherent Overcharge Protection

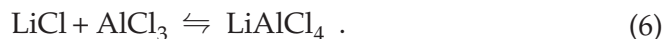
Among the various rechargeable lithium battery systems, only the lithium cells [4] using solutions of inorganic salts such as LiAlCl₄ or LiGaCl₄ in sulfur dioxide as electrolytes were found to have inherent overcharge protection. On overcharge, lithium is deposited at the negative electrode and AlCl₄⁻ is oxidized at the positive electrode to form AlCl₃ and Cl₂ as shown by



Both aluminum chloride and chlorine were found to be soluble in the inorganic electrolyte, and chlorine diffuses to the negative electrode and reacts with lithium to form lithium chloride, which then combines with aluminum chloride to regenerate lithium tetrachloroaluminate according to the reactions



and



Thus, rechargeable lithium cells using solutions of inorganic salts such as LiAlCl₄ or LiGaCl₄ in sulfur dioxide electrolyte are inherently protected against overcharge.

3. Electrolyte Additives for Overcharge Protection in Lithium and Lithium-Ion Cells

Most of the lithium and lithium-ion cells that have been proposed for various applications are not inherently protected against overcharge. Thus, the overcharge leads to the degradation of the electrolyte due to solvent oxidation and results in poor cycle life and premature failure of these cells. Attempts have been made to provide in situ overcharge protection in these cells by the use of electrolyte additives that provide an electrochemical shuttle to absorb the excess charge. The electrolyte additive is oxidized during overcharge, and the oxidation product diffuses to the negative electrode and reacts with lithium metal to regenerate the original electrolyte additive. The oxidation potential of the additive is below the solvent oxidation potential, so that it prevents the oxidation of the solvent and provides overcharge protection in these cells. Several electrolyte additives have been proposed for providing overcharge protection in lithium cells. A detailed discussion of these additives is presented below.

3.1 Lithium Halides

The use of lithium iodide as an electrolyte additive to provide overcharge protection in lithium cells was first suggested by Holleck et al [5,6]. These investigators proposed that lithium iodide would be oxidized to iodine at less positive potentials and thereby prevent the oxidation of organic solvents. The iodine generated at the positive electrode would then react with lithium metal to regenerate lithium iodide. Therefore, the LiI/I_2 reaction mechanism would provide overcharge protection to rechargeable lithium organic electrolyte batteries.

The oxidation of lithium halides has been studied [7,8] in tetrahydrofuran solutions, and the oxidation of the halide ion (X^-) was found to be a two-step reaction:



and



It was found that lithium iodide is oxidized to lithium triiodide and iodine at potentials well below the oxidation potential of tetrahydrofuran and, thus, can be effectively used as an electrolyte additive to provide overcharge protection to rechargeable lithium cells such as $\text{Li}/\text{LiAsF}_6\text{-tetrahydrofuran}/\text{TiS}_2$. Both lithium triiodide and iodine formed by the oxidation of lithium iodide would then react with the lithium negative electrode to regenerate lithium iodide. However, it was also found that the formation of iodine in these solutions causes the polymerization of tetrahydrofuran. Therefore, to prevent this polymerization, it is necessary to use excess lithium iodide so that any iodine formed

is immediately complexed by lithium iodide to form lithium triiodide according to the reaction



Lithium bromide was also found to undergo two-step oxidation in LiAsF_6 -tetrahydrofuran solutions to lithium tribromide and bromine. However, both lithium tribromide and bromine were found to cause the polymerization of tetrahydrofuran; thus, it was concluded that lithium bromide was not a useful electrolyte additive to provide overcharge protection in Li/LiAsF_6 -tetrahydrofuran/ TiS_2 cells.

Abraham et al [9] demonstrated the usefulness of lithium halide additives to provide overcharge protection in Li/LiAsF_6 -tetrahydrofuran:2-methyl tetrahydrofuran (50:50 vol%)/ TiS_2 cells. However, the presence of either lithium iodide or lithium bromide in the electrolyte had a deleterious effect on the cycling efficiency of lithium even under normal cycling conditions. The decrease in lithium cycling efficiency was attributed to the adsorption of halides on a lithium anode surface, which led to deterioration in the morphology of the plated lithium.

3.2 Metalloenes

Several metallocenes that oxidize at potentials in the range from 1.7 to 3.5 V have been identified [10–12] as suitable electrolyte additives for providing overcharge protection in lithium cells. During overcharge, the metallocenes are oxidized to a positively charged species that then diffuses to the negative electrode and is reduced by lithium to regenerate the original metallocene. Abraham et al [10] used a 0.5-molar solution of n-butylferrocene additive in an electrolyte consisting of a 1.5-molar solution of lithium hexafluoroarsenate in tetrahydrofuran:2-methyl tetrahydrofuran:2-methylfuran (48:48:4 vol%) to demonstrate the overcharge protection in Li/TiS_2 cells. The cells with the additive attained a steady voltage potential of 3.25 V on overcharge, whereas the cells without the n-butylferrocene additive had increased voltage to upwards of 5.0 V.

Golovin et al [11] investigated the use of ferrocene and its derivatives as electrolyte additives in 1.5 molar solutions of lithium hexafluoroarsenate in propylene carbonate:ethylene carbonate (50:50 vol%) to provide overcharge protection. The effectiveness of these additives in providing overcharge protection was successfully demonstrated in AA-size $\text{Li}/\text{Li}_x\text{MnO}_2$ cells.

3.3 Tetramethyl-p-phenylenediamine

Halpert et al [13] evaluated the use of tetracyanomethane and tetramethyl-p-phenylenediamine as electrolyte additives in 1.5-molar LiAsF_6 solutions in ethylene carbonate: 2-methyl tetrahydrofuran: mixed furans

(10:88:2 vol%) to provide overcharge protection in Li/TiS₂ cells. They found that only tetramethyl-p-phenylenediamine provided limited overcharge protection in these cells.

3.4 Polypyridines

Cha et al [14] investigated the use of iron complexes 2,2'-bipyridyl and 1,10-phenanthroline as electrolyte additives in 1.0-molar lithium perchlorate solution in propylene carbonate-dimethoxyethane (50:50 vol%). Electrolyte solutions containing a 20-mg/ml of Fe(bpy)₃-ClO₄)₂ complex provided overcharge protection in lithium-ion cells using composite dimensional manganese oxide and Li_xMn₂O₄ as positive electrodes.

3.5 Biphenyl

H. Mao and U. von Sacken [15] have taken a slightly different approach to protect lithium-ion cells from overcharge. They did not provide an electrochemical shuttle mechanism for overcharge protection but instead used aromatic compounds such as biphenyl (2 wt%) to protect the lithium-ion cells from overcharge abuse. The aromatic compounds undergo electrochemical polymerization at the abnormally high voltages reached during overcharge and generate gases. The increase in pressure as a result of the gases activates pressure-sensitive internal electrical disconnect devices. This makes the cells inoperative and, thus, protects them from any overcharge abuse.

3.6 Organic Compounds

Richardson and Ross [16] investigated a number of redox shuttle electrolyte additives for overcharge protection in lithium-polymer electrolyte cells. Among the compounds studied, tricyanobenzene, tetracyanoquinodimethane, sodium triazole, and sodium imidazole were found to perform well in providing overcharge protection in Li/polyethylene oxide-lithium trifluoromethanesulfonimide/Li_{2+x}Mn₄O₉ cells.

4. Cathode Additives for Overcharge Protection in Lithium Cells

Huang et al [17] have suggested the use of a transition metal oxide such as $\text{Li}_2\text{Mn}_2\text{O}_4$ as a cathode additive to provide overcharge protection in lithium cells. The cathode additive is charged at a slightly higher voltage than the characteristic charge cutoff voltage of the cathode of the cell. Thus, the cathode additive is oxidized during overcharge and provides some protection to the cell.

5. Conclusions

The literature survey shows that among all the lithium and lithium-battery systems investigated, only the rechargeable lithium batteries [4] using solutions of inorganic salts in sulfur dioxide as electrolytes have an inherent mechanism that provides overcharge protection. For other low-voltage rechargeable lithium battery systems such as lithium/titanium disulfide, a number of electrolyte additives [5–14,16] are available that would form an electrochemical shuttle during overcharge and provide overcharge protection in these cells. It appears likely that none of the shuttles identified so far will be fully practical in terms of long service life, reasonably high rates of recombination, or the avoidance of side reactions with the other cell components.

A thorough search of the literature did not reveal any method to provide overcharge protection in lithium-ion batteries. Present formulations of lithium-ion batteries use relatively high-potential cathode materials (i.e., lithium-intercalated cobalt, nickel, or manganese oxides) and require charging to a potential of ~ 4.25 V. There are no satisfactory concepts in the literature for an electrolyte additive that would be the basis of an electrochemical shuttle operable at potentials higher than 4.25 V versus Li. Alternatives to awaiting a breakthrough in this area are to turn to lower-potential cathodes or to continue to rely on cell-monitoring techniques.

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